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(54) [Title of the Invention] METHOD OF PRODUCING METALLIC PARTICLE POWDER

(57) [Abstract]

[Problem]

The present invention relates to a method of producing metallic particle powder that permits obtaining dense, highly pure spherical metallic particle powder of superior dispersibility.

[Means of Solution]

A method of producing metallic particle powder, in which spherical metallic particle powder is obtained by spray pyrolysis using an aqueous solution of nickel acetate, an aqueous solution of nickel formate, an aqueous solution of copper acetate, or an aqueous solution of copper formate as a spray pyrolysis solution.

[Claims]
[Claim 1]

A method of producing metallic particle powder, in which spherical metallic particle powder is obtained by spray pyrolysis using an aqueous solution of nickel acetate, an aqueous solution of nickel formate, an aqueous solution of copper acetate, or an aqueous solution of copper formate as a spray pyrolysis solution.

[Detailed Explanation of the Invention]

[0001]

[Field of Industrial Application]

The present invention relates to a method of producing metallic particle powder that allows for obtaining dense, highly pure spherical metallic particle powder of superior dispersibility.

[0002]

[Prior Art]

As a result of advances in the miniaturization, performance enhancement and weight reduction of electronic devices in recent years, there is demand for further improvements in the field of metallic particle powders used for electronic device components, such as, for instance, laminated capacitors and other polar materials.

[0003]

In particular, nickel particle powders and copper particle powders used for the above-described applications are required to be agglomeration-free, possess superior dispersibility, and be very dense and highly pure.

[0004]

On the other hand, as is well known, the spray pyrolysis process is one of the methods used for producing spherical metallic particle powders.

[0005]

The spray pyrolysis process is a method, in which target particle powders are obtained via pyrolysis by atomizing a raw material solution into microscopic droplets using a nozzle or ultrasonic waves and then evaporating the solvent from the droplets.

[0006]

In the past, methods described in Japanese Unexamined Patent Application Publication No. Hei 8-170112, Japanese Unexamined Patent Application Publication No. Hei 11-80818 and Japanese Unexamined Patent Application Publication No. Hei 11-236607 have been known as methods used for obtaining nickel particle powders and other metallic particle powders by the spray pyrolysis technique.

[0007]

[Problems the Invention Seeks to Overcome]

The industrial manufacture of spherical nickel particle powders and spherical copper particle powders disclosed in the previous publications is associated with a number of problems, such as the ones indicated below.

[0008]

Namely, Japanese Unexamined Patent Application Publication No. Hei 8-170112 describes a process, in which spray pyrolysis is carried out in a specific heating temperature range. However, the flow rate of the carrier gas in that specific heating temperature range and other residence time parameters are not taken into consideration and it is difficult to industrially produce dense spherical nickel particle powders and spherical copper particle powders of uniform size.

[0009]

In addition, the spray pyrolysis process described in Japanese Unexamined Patent Application Publication No. Hei 11-80818 is unsuitable for industrial purposes because it makes use of a carrier gas containing 1~35 vol% of a reducing gas (16.7 vol% in the embodiments).

[0010]

Also, in the spray pyrolysis process described in Japanese Unexamined Patent Application Publication No. Hei 11-236607, metallic particle powder is manufactured without utilizing a reducing gas by means of complex formation using ammonia or hydrogen peroxide solutions as additives. However, the process is difficult to implement industrially because it requires complex formation.

[0011]

Furthermore, Japanese Unexamined Patent Application Publication No. Hei 3-131560 describes a process, in which superconductors are manufactured by obtaining metal oxide particle powders by spray pyrolysis of various metal powders making up the superconductor and then heating and sintering them. However, no consideration is given to the fact that copper oxide (CuO) is obtained by means of spray pyrolysis using copper acetate ($Cu(CH_3COO)_2$) as a copper compound and oxygen as a carrier gas and a metal particular powder is obtained under a reducing atmosphere.

[0012]

Thus, the technical problem solved by the present patent consists in the industrial manufacture of dense, highly pure spherical metallic particle powder of superior dispersibility by the spray pyrolysis process.

[0013]

[Means for Overcoming the Problems]

The present invention solves the above-mentioned technical problem in the following manner.

[0014]

Namely, the present invention is a method of producing metallic particle powder, in which spherical metallic particle powder is obtained by spray pyrolysis using an aqueous solution of nickel acetate, an aqueous solution of nickel formate, an aqueous solution of copper acetate, or an aqueous solution of copper formate as a spray pyrolysis solution.

[0015]

The constitution of the present invention is described in detail below.

[0016]

The spray pyrolysis solution used in the present invention is an aqueous solution of nickel acetate, an aqueous solution of nickel formate, an aqueous solution of copper acetate, or an aqueous solution of copper formate. Conducting spray pyrolysis using the above-mentioned aqueous solutions makes allows for obtaining the target spherical metallic particle powders while making it possible to decrease the amount of the reducing gas introduced in the carrier gas.

[0017]

The concentration of the spray pyrolysis solution is preferably 0.001~0.5 mol/L. Concentrations lower than 0.001 mol/L are undesirable because the particle size of the resultant spherical metallic particle powder becomes too small. Concentrations in excess of 0.5 mol/L are undesirable because the particle size increases and the particle size distribution tends to deteriorate. More preferably, the concentration is 0.005~0.4 mol/L.

[0018]

Because in the spray pyrolysis process the size of the resultant particles of the metallic particle powder varies depending on the size of the liquid droplets produced by atomization, atomization is carried out such that the size of the liquid droplets is made uniform. Specifically, in

this process, liquid droplets can be formed using a 2-fluid nozzle, ultrasonic waves, static electricity, or other methods, but it is preferable to carry out the atomization using ultrasonic waves.

[0019]

The resultant liquid droplets are introduced into a heating furnace using a carrier gas containing a reducing gas. Although hydrogen gas, CO gas, ammonia gas, etc. can be used as the reducing gas, hydrogen is more preferable from an industrial standpoint. Although there are no particular limitations concerning the carrier gas as long as it is inert, the carrier gas is preferably nitrogen.

[0020]

The present invention makes it possible to use a smaller amount of the reducing gas because of using an aqueous solution of an acetic acid salt or an aqueous solution of a formic acid salt. The concentration of the reducing gas is preferably less than 1.0 vol%, and, more preferably, not more than 0.9 vol%.

[0021]

The flow rate of the carrier gas is preferably 1.0~10 cm/sec.

[0022]

The heating furnace is preferably provided with 5 or more zones, and, preferably, with a temperature gradient such that the highest temperature is reached after the third zone. When heating at high temperatures starts from the first zone, it is difficult to obtain dense spherical metallic particle powders due to the resultant violent reactions.

[0023]

The specific temperatures used in the heating furnace are 200~400°C for the first zone, 450~650°C for the second zone, and 750~1000°C for the third and higher zones.

[0024]

In addition, the ratio L/D of the length L of the first zone of the heating furnace to the diameter D of its core tube is preferably not less than 5. When the L/D ratio is less than 5, the particle size distribution of the resultant spherical metallic particle powder deteriorates because the time of residence in a heating furnace is shortened. When industrial productivity is taken into account, the upper limit value of the L/D ratio is 50.

[0025]

Metallic particle powder obtained upon completion of pyrolysis is collected using an electrical precipitator etc. by regular methods.

[0026]

Nickel particle powders obtained in accordance with the present invention are spherical in shape and have an average particle size of 0.01~1.0 μm (if necessary, it can be adjusted to 0.05~0.8 μm), a geometric standard deviation value of not more than 2.0 (if necessary, it can be adjusted to 1.8 or less), a BET specific surface area value of 1~100 m^2/g (if necessary, it can be adjusted to 1.5~80 m^2/g), a density ratio of 0.75~1.0 (if necessary, it can be adjusted to 0.8~1.0), and a volume inherent resistivity value of 1.0~9.5×10^3 Ω·cm (if necessary, it can be adjusted to 1.0~5.0×10^3 Ω·cm). In addition, the crystallinity is not less than 4000.

[0027]

Copper particle powders obtained in accordance with the present invention are spherical in shape and have an average particle size of 0.01~1.0 μm (if necessary, it can be adjusted to 0.05~0.8 μm), a geometric standard deviation value of not more than 2.0 (if necessary, it can be adjusted to 1.8 or less), a BET specific surface area value of 1~100 m^2/g (if necessary, it can be adjusted to 1.5~80 m^2/g), a density ratio of 0.75~1.0 (if necessary, it can be adjusted to 0.8~1.0), and a volume inherent

resistivity value of $1.0\sim9.5\times10^3$ Ω·cm (if necessary, it can be adjusted to $1.0\sim5.0\times10^3$ Ω·cm). In addition, the crystallinity is not less than 4000.

[0028]

[Embodiments of the Invention]

A representative embodiment of the present invention is described below.

[0029]

The average particle size of the particle powders was represented by an average value obtained by measuring the diameters of approximately 350 particles shown in a photograph produced by enlarging an electron microscope photograph (×20,000) four times in the vertical and horizontal direction.

[0030]

The geometric standard deviation of the particle size of the particle powders was represented by a value obtained by the following method. Namely, the number and actual particle diameters of particles calculated from measurement values produced by measuring the diameters of the particles shown in the above-mentioned enlarged photograph were used in a statistical technique, in which the particle sizes were plotted along the X-axis on logarithmic normal probability paper and the cumulative numbers (cumulative undersizes) of particles belonging to predetermined particle size ranges were plotted along the Y-axis as percentages. Subsequently, particle size values corresponding to cumulative numbers of 50% and 84.13% were read from the graph, and the deviation was obtained as a value computed in accordance with the following formula: geometric standard deviation value = (particle size at cumulative undersize of 84.13%) / (particle size at cumulative undersize of 50% (geometric mean diameter)). The closer the geometric standard deviation value comes to 1, the better the gradation of the particle size of the particles is.

[0031]

The specific surface area values were represented by values determined by the BET method.

[0032]

The densities of the powders were measured using the "MultiVolume Pycnometer 1305" (from Micromeritics Instrument Corporation) and the density ratios of the powders were obtained as ratios to the true density of the metal powders (Ni = 8.845 g/cm^3, Cu = 8.92 g/cm^3).

[0033]

An X-ray diffractometer RAD-IIA (from Rigaku Industrial Corporation) was used for measurement, with 2θ ranging from 3 to 105°, and the peak intensity of the strongest line was used as the crystallinity of the metallic particle powders.

[0034]

To determine the volume inherent resistivity of the metallic particle powders, first of all, 0.5g of a sample particle powder was weighed and pressure formed under a pressure of 1.372×10^7 Pa (140 kg/cm^2) in a KBr tablet maker (from Shimadzu Corporation).

[0035]

Next, for over 12 hours, the sample to be analyzed (cylindrical in shape) was exposed to an environment with a temperature of 25°C and a relative humidity of 60%, after which the sample to be analyzed was placed between stainless steel electrodes and its resistance value R (Ω) was measured by applying a voltage of 15V using a Wheatstone bridge (TYPE 2768, from Yokogawa Hokushin Electric Corporation).

[0036]

Next, the surface area A (cm^2) of the top face and thickness t_0 (cm) of the sample to be analyzed were measured and the volume inherent resistivity value ($\Omega \cdot cm$) was obtained by substituting the respective measured values in Formula 1.

[0037]

[Formula 1]

Volume inherent resistivity value ($\Omega \cdot cm$) = $R \times (A/t_0)$

Here, R was the actual measured resistance value.

[0038]

<Production of spherical metallic particle powder>

500 ml of an aqueous solution of nickel formate with a concentration of 0.15 mol/L was placed in an ultrasonic atomizer. The ultrasonic wave intensity was set to 50 mW, and, upon confirmation of aerosol formation above the surface of the aqueous solution of nickel formate, nitrogen gas containing 0.5 vol% of hydrogen gas was used as a carrier gas to introduce the aerosol into a ceramic heating furnace at a flow rate of 5 cm/sec inside the tube. In addition, the L/D ratio of the heating furnace was 30.

[0039]

The heating temperatures used in zones 1 through 5 of the heating furnace were respectively 300°C, 600°C, 800°C, 800°C and 800°C. After gradually evaporating the solvent from the aerosol, it was subjected to heat treatment that produced pyrolytic reactions in the aerosol. Particles were collected by placing an electrical precipitator at the exit end of the heating furnace. At such time, aerosol at the inlet of the precipitator was subjected to corona discharge treatment using a direct current voltage of 5000V to charge the particles and raise the efficiency of particle collection by the electrical precipitator.

[0040]

The resultant nickel particle powder was spherical in shape, with an average particle size of 0.25 μm, a geometric standard deviation value of 1.44, a BET specific surface area value of 9.8 m^2/g, a density ratio of 0.88, a volume inherent resistivity value of 2.3×10^2 $\Omega \cdot cm$, and a crystallinity of 8700.

[0041]

FIG. 1 shows an electron microscope photograph (×100,000) of the spherical nickel particle powder obtained above. The photograph confirms that a true spherical particulate was obtained.

[0042]

[Operation]

The most important feature of the present invention consists in is the fact that the use of an aqueous solution of nickel acetate, an aqueous solution of nickel formate, an aqueous solution of copper acetate, or an aqueous solution of copper formate as a spray pyrolysis solution makes it possible to decrease the amount of the reducing gas and obtain dense, highly pure spherical metallic particle powders of superior dispersibility.

[0043]

The present inventors believe that the reason why it makes the reduction in the amount of the reducing gas possible consists in the production of reducing CO gas during the pyrolysis of nickel acetate, nickel formate, copper acetate, or copper formate.

[0044]

In addition, it is believed that production of dense particle powders that are spherical, have superior particle size distribution, and do not contain hollow particles is made possible by the fact that in the present invention temperature regulation is performed more precisely by providing more

zones in the heating furnace and is carried out in such a manner that the highest temperature is reached after the third zone of the heating furnace.

[0045]
[Application Examples]

Application examples and comparative examples are provided below.

[0046]

Application Examples 1~4, Comparative Examples 1~5

With the exception of changing the type of the starting raw material, the concentration of the raw material solution, the type and flow rate of the carrier gas, the type and concentration of the reducing gas, and the temperature and L/D ratio of the heating furnace, spherical metallic particle powders were obtained in the same manner as in the above-described embodiment.

[0047]

The manufacturing conditions used in the production of the powders are listed in Table 1 and the characteristics of the resultant spherical metallic particle powders are listed in Table 2.

[0048]
[Table 1]

Application Examples and Comparative Examples	Type of starting raw material	Concentration of raw material solution (mol/L)	Metallic Particle Powder Manufacturing Conditions									
			Carrier Gas		Reducing Gas		Temperature of Heating Furnace					L/D
			Type	Flow rate (cm/sec)	Type	Concentration (vol%)	1st zone (°C)	2nd zone (°C)	3rd zone (°C)	4th zone (°C)	5th zone (°C)	(—)
Application Example 1	Nickel acetate	0.1	Nitrogen gas	7.5	Hydrogen gas	0.5	300	600	850	850	850	30
" 2	Nickel formate	0.1	"	10.0	"	0.9	200	500	800	800	800	30
" 3	Copper acetate	0.2	"	5.0	"	0.3	350	550	850	850	850	20
" 4	Nickel acetate	0.01	"	2.0	"	0.1	250	500	800	850	850	50
Comparative Example 1	Nickel sulfate	0.1	"	5.0	"	0.5	300	500	750	750	750	30
" 2	Nickel nitrate	0.1	"	5.0	"	0.5	300	500	750	750	750	30
" 3	Nickel chloride	0.1	"	5.0	"	0.5	300	500	750	750	750	30
" 4	Nickel sulfate	0.1	"	5.0	"	0.5	800	800	800	800	800	30
" 5	Nickel sulfate	0.1	"	5.0	"	0.5	300	500	750	750	750	30

[0049]
[Table 2]

Application Examples and Comparative Examples	Characteristics of Metallic Particle Powders							
	Type of metallic particle	Shape	Average particle size (μm)	Geometric standard deviation value (—)	BET specific surface area (m^2/g)	Density ratio (—)	Crystallinity (—)	Volume inherent resistivity value (Ω·cm)
Application Example 1	Nickel	Spherical	0.21	1.46	10.6	0.83	8600	8.6×10^2
" 2	"	Spherical	0.18	1.38	21.8	0.85	8500	3.2×10^2
" 3	Copper	Spherical	0.36	1.66	6.4	0.84	8800	1.6×10^3
" 4	Nickel	Spherical	0.02	1.53	56.5	0.90	8100	1.8×10^2
Comparative Example 1	Nickel	Spherical	0.36	1.71	7.6	0.66	5400	5.6×10^4
" 2	Nickel	Spherical	0.28	1.86	8.2	0.72	6300	8.3×10^4
" 3	Nickel	Granular	0.56	2.26	3.6	0.34	2400	$2.4 \times 10^{\cdots}$
" 4	Nickel	Spherical	0.26	1.96	9.2	0.54	6300	3.6×10^5
".5	Nickel	Spherical	0.25	1.93	8.3	0.62	7100	6.8×10^4

[0050]

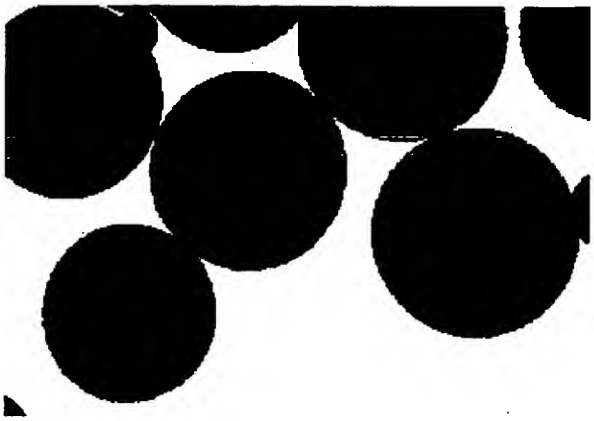
[Effects of the Invention]

The present invention makes it easy to industrially produce dense, highly pure spherical metallic particle powders of superior dispersibility.

[Brief Description of the Drawings]

[FIG.1]

A scanning electron microscope photograph (×100,00) showing the shape of the particles of a nickel particle powder obtained in an embodiment of the present invention.



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